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$$\frac{1}{r} - r < |w| < \frac{1}{r} + r$$

for  $|z| = r$ ,  $0 < r < 1$ , except when

$$w = \frac{1}{z} + e^{2\alpha i} z$$

with  $\alpha$  real, the upper and lower bounds of  $|w|$  being then reached when  $z = \pm e^{-\alpha i} r$  and  $z = \pm i e^{-\alpha i} r$ , respectively. This particular function maps  $|z| < 1$  on the  $w$ -plane cut along the straight line from  $w = -2e^{\alpha i}$  to  $w = 2e^{\alpha i}$ .

<sup>1</sup> Koebe, *Göttingen, Nachr. Ges. Wiss.*, 1909 (73).

<sup>2</sup> Gronwall, *Paris, C. R. Acad. Sci.*, **162**, 1916 (249).

<sup>3</sup> Gronwall, *Ibid.*, **162**, 1916 (316).

<sup>4</sup> Fricke and Klein, *Vorlesungen über die Theorie der automorphen Functionen*, II, Leipzig, 1912 (497).

<sup>5</sup> Gronwall, *Annals Math., Princeton*, Ser. 2, **16**, 1914 (74).

## ON THE CONNECTION OF THE SPECIFIC HEATS WITH THE EQUATION OF STATE OF A GAS\*

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Read before the Academy, April 26, 1920

One would suppose that this subject was already exhausted, but I am disposed to believe that such is not the case. In these PROCEEDINGS, 5, July, 1919 (286-288) I published a paper "On the Possible Form of the Equation of State of Powder Gases." In a private letter from M. LeChatelier, in commenting on this paper, he says: "Votre objection au sujet de nos chaleurs spécifiques nous était venue à l'esprit, mais nous pensions avoir démontré, en partant des principes de la thermodynamique, que toutes les fois qu'un fluide obéit à une équation caractéristique de la forme

$$V = F(P/T)$$

les chaleurs spécifiques sont indépendantes de la pression."

I do not find where, if anywhere, M. LeChatelier has published this conclusion. Certainly it is not in the great paper by Mallard and LeChatelier, *Journal de Physique*, Ser. 2, 4 (59-84), "Recherches sur la Combustion des Mélanges Gazeux Explosifs," where the matter is not mentioned. In a paper published in the *Physical Review*, 29, No. 3, September, 1909, "On the Definition of an Ideal Gas," written by me, but suggested by my then colleague Professor Rosanoff, and published under our joint names, I have investigated the properties of a gas having the equation of state mentioned by M. LeChatelier, but have said nothing about the specific heats. Inasmuch as the matter seems to be not quite

\* Contribution from the Ballistic Institute, Clark University, No. 8.

clear and inasmuch as in the five-foot shelf of treatises on thermodynamics in my library I cannot find the answer to the question that I have in mind, I think it worth while to take the matter up *ab initio*. To be sure my colleague Professor Charles A. Kraus has pointed out to me that van der Waals, in his excellent *Lehrbuch der Thermodynamik*, Kap. II, has partially treated the subject, and Professor Gilbert N. Lewis, whom I met yesterday on the Avenue, referred me to the same "well-known formula," and intimated that there was nothing more to be added. I am not quite convinced. After teaching thermodynamics for thirty years I find it is only now that my ideas on some points are becoming clarified.

Let us suppose any system to be specified by two coördinates,  $x$  and  $y$ , in terms of which all thermal data may be expressed, neither being the temperature. If we deal with unit of mass of a substance, the specific heat at constant  $x$  is defined by the equation

$$dQ_x = C_x dT_x,$$

where  $dT_x$  is the change of temperature made when  $x$  is constant and  $dQ$  is the amount of heat required for a change of state. Similarly for the specific heat at constant  $y$ :

$$dQ_y = C_y dT_y,$$

Now we have in any change

$$dT = \frac{\partial T}{\partial x} dx + \frac{\partial T}{\partial y} dy,$$

and consequently:

$$dQ_x = C_x \frac{\partial T}{\partial y}, \quad dQ_y = C_y \frac{\partial T}{\partial x} dx.$$

Since for an infinitesimal change the total amount of heat required is the sum of the two preceding, we have for any change whatever

$$dQ = C_y \frac{\partial T}{\partial x} dx + C_x \frac{\partial T}{\partial y} dy.$$

But, by the first law of thermodynamics, when we are dealing with a system under a uniform normal pressure  $p$  we have

$$dQ = dU + p dv$$

where  $U$  is the intrinsic energy of the substance. Writing out the perfect differentials  $dU$  and  $dv$  in terms of  $dx$  and  $dy$ , which are independent, we have the two partial differential equations:

$$\begin{aligned} \frac{\partial U}{\partial x} &= C_y \frac{\partial T}{\partial x} - p \frac{\partial v}{\partial x}, \\ \frac{\partial U}{\partial y} &= C_x \frac{\partial T}{\partial y} - p \frac{\partial v}{\partial y}. \end{aligned}$$

From these, eliminating  $U$  by cross differentiation, we get:

$$\frac{\partial C_x}{\partial x} \frac{\partial T}{\partial y} - \frac{\partial C_y}{\partial y} \frac{\partial T}{\partial x} + (C_x - C_y) \frac{\partial^2 T}{\partial x \partial y} = \frac{\partial(p, v)}{\partial(x, y)} \quad (1)$$

From the second law of thermodynamics, introducing the integrating factor  $1/T$  and the entropy  $S$ , we have

$$\frac{dQ}{T} = dS = \frac{\partial S}{\partial x} dx + \frac{\partial S}{\partial y} dy = \frac{C_y}{T} \frac{\partial T}{\partial x} dx + \frac{C_x}{T} \frac{\partial T}{\partial y} dy$$

from which we get in a similar manner:

$$\frac{\partial C_x}{\partial x} \frac{\partial T}{\partial y} - \frac{\partial C_y}{\partial y} \frac{\partial T}{\partial x} + (C_x - C_y) \frac{\partial^2 T}{\partial x \partial y} = \frac{(C_x - C_y)}{T} \frac{\partial T}{\partial x} \frac{\partial T}{\partial y} \quad (2)$$

By a combination of these two equations we get

$$(C_x - C_y) \frac{\partial T}{\partial x} \frac{\partial T}{\partial y} = T \frac{\partial(p, v)}{\partial(x, y)}$$

which is equation (3) of my paper quoted above.

These are all the equations that we can get from the laws of thermodynamics and since any function has two partial derivatives for  $C_x$  and  $C_y$ , there will be four, which to be sure are connected by two equations. It is, I think, obvious that two equations are not sufficient. At any rate, let us proceed to an examination of the equation of state suggested by M. LeChatelier. If we have:

$$x = p, \quad y = v, \quad T = pf(v) = xf(y),$$

we at once obtain

$$\frac{\partial T}{\partial x} = f(y), \quad \frac{\partial T}{\partial y} = xf'(y), \quad \frac{\partial^2 T}{\partial x \partial y} = f'(y)$$

And accordingly in the equation of the first law we have

$$xf'(y) \frac{\partial C_x}{\partial x} - f(y) \frac{\partial C_y}{\partial y} + (C_x - C_y) f'(y) = 1. \quad (3)$$

and in the equation of the second law

$$xf'(y) \frac{\partial C_x}{\partial x} - f(y) \frac{\partial C_y}{\partial y} + (C_x - C_y) f'(y) = (C_x - C_y) f'(y). \quad (4)$$

We accordingly obtain the relations between the two specific heats:

$$xf'(y) \frac{\partial C_x}{\partial x} - f(y) \frac{\partial C_y}{\partial y} = 0, \quad (5)$$

$$C_x - C_y = \frac{1}{f'(y)}. \quad (6)$$

From (6) we get

$$\frac{\partial C_y}{\partial y} = \frac{\partial C_x}{\partial y} + \frac{f''}{f'^2}. \quad (7)$$

Substituting this value in equation (5) we obtain,

$$x \frac{f'}{f} \frac{\partial C_x}{\partial x} - \frac{\partial C_x}{\partial y} = \frac{f''}{f'^2}, \quad (8)$$

a partial differential equation of the first order for  $C_x$ , which is of the form

$$P \frac{\partial z}{\partial x} + Q \frac{\partial z}{\partial y} = R$$

if we put,

$$C_x = z, \quad P = x \frac{d \log f(y)}{dy}, \quad Q = -1, \quad R = -\frac{d}{dy} \left( \frac{1}{f'} \right).$$

This is immediately integrated by Lagrange's method, if we write

$$\frac{dx}{P} = \frac{dy}{Q} = \frac{dz}{R}, \quad \frac{dx}{x \frac{d \log f}{dy}} = -dy = -\frac{dz}{\frac{d}{dy} \left( \frac{1}{f'} \right)}.$$

We obtain two particular integrals, in which we are to put

$$u \equiv xf = T = \text{const.}, \quad v \equiv z - \frac{1}{f'} = \text{const.}, \quad v = \varphi(u),$$

where  $\varphi$  is an arbitrary function. We thus obtain finally

$$C_p = 1/f'(v) + \varphi(T), \quad C_v = \varphi(T) \quad (9)$$

and we find that neither of the specific heats is constant or independent of the pressure, nor is their difference constant, although it is independent of the pressure. Such a gas has no cohesion pressure, but does not in general have a zero Joule-Kelvin effect. If, on the contrary, we take a gas subject to the equation,

$$T = vg(p)$$

which has a zero Joule-Kelvin effect, we have a similar conclusion, interchanging  $p$  and  $v$ .

If, on the other hand, one of our variables is the absolute temperature, we are to write,

$$dQ = C_x dT + L_x dx \quad (10)$$

where  $L_x$  is the latent heat for constant  $x$ . We then obtain from the first law

$$\begin{aligned} \frac{\partial U}{\partial x} &= L_x - p \frac{\partial v}{\partial x}, \quad \frac{\partial U}{\partial T} = C_x - p \frac{\partial v}{\partial T}, \\ \frac{\partial C_x}{\partial x} - \frac{\partial L_x}{\partial T} &= \frac{\partial(p, v)}{\partial(x, T)}, \end{aligned} \quad (11)$$

and from the second,

$$\begin{aligned} \frac{\partial S}{\partial x} &= \frac{L_x}{T}, \quad \frac{dS}{dT} = \frac{C_x}{T} \\ \frac{\partial C_x}{\partial x} - \frac{\partial L_x}{\partial T} &= -\frac{L_x}{T}, \end{aligned} \quad (12)$$

and combining the two,

$$\frac{L_x}{T} = - \frac{\partial(p, v)}{\partial(x, T)} \quad (13)$$

which is the generalized Clapeyron-Clausius equation. Making use of this in (11) we obtain the "well-known equation" mentioned by Professor Lewis, and given by van der Waals, p. 52:

$$\frac{\partial C_v}{\partial v} = T \frac{\partial^2 p}{\partial T^2}$$

Applying this to the case mentioned by Professor Lewis,

$$p = \varphi_1(v) + T\varphi_2(v)$$

which is the case under which van der Waals' familiar equation comes, we find, to be sure, that  $C_v$  is independent of the *volume*, but on solving for  $T$ , and writing

$$T = pV_1(v) + V_2(v)$$

and applying equations (1) and (2), we do not find anything particularly simple for  $C_p$ .

All this is very simple, but what I wish to call attention to is that in any case, the specific heats being defined by a partial differential equation of the first order, there is one perfectly arbitrary function, by no means necessarily of the temperature. In any case I believe that the teaching of thermodynamics by means of the equation of the so-called ideal gas or by means of van der Waals' equation is by no means conducive to clearness.

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## ANOMALOUS OSMOSE

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It has repeatedly been noted that solutions of electrolytes with different types of "semi-permeable" membranes give osmotic pressure values quite different in magnitude from the calculated maximum values derived from the gas law formulations. We may define *normal osmotic pressure values* as those which conform to the gas law formulations. We have an example of this type when a solution of cane sugar is used with a semi-permeable membrane such as copper ferrocyanide. *Anomalous osmotic pressure values* are those which do not conform to the gas law formulations; they may be greater or less than the normal values. The abnormality of the effects may be of considerable magnitude and may even result in so-called negative osmose, in which case the direction of flow of liquid is from the concentrated to the more dilute solution.

\* Communicated by M. Gomberg, April 20, 1920